

## Timescales for migration of atmospherically derived sulphate through an alpine/subalpine watershed, Loch Vale, Colorado

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**Abstract.** Sulphur 35, a cosmogenically produced radioisotope with a short half-life (87 days), was measured in snowpack during 1993–1997 and at four locations within the Loch Vale watershed during 1995–1997. The four sites include the two main drainages in the watershed, Andrews Creek and Icy Brook, a small south facing catchment flowing into Andrews Creek (Andrews Spring 1), and a similar north facing catchment flowing out of a scree field into Icy Brook (Spring 19). Concentrations ranged from a high of almost 50 mBq/L for a sample from Spring 19 in June 1996 to a concentration near the detection limit for a sample from Andrews Creek in April 1997. Sulphur 35 concentrations were normalized to sulphate (as mBq/mg  $\text{SO}_4^{2-}$ ) and were decay-corrected to a Julian day of 90 (April 1) for each year. Snowpack had the highest  $^{35}\text{S}$  concentration with an average concentration of 53 mBq/mg  $\text{SO}_4^{2-}$ . Concentrations in the streams were much lower, even when corrected for decay relative to JD 90. The large  $^{35}\text{S}$  concentrations found in Spring 19 were the result of increases in concentration due to sublimation and/or evapotranspiration and were lower than snowpack when normalized to sulphate. Using  $^{35}\text{S}$  concentrations found in snowpack as of JD 90 as a beginning concentration, the fraction of sulphate in streamflow that was derived from atmospheric deposition within the prior water year was estimated. For Icy Brook and Andrews Creek the fraction of the sulphate in streamflow derived from that year's snowpack and precipitation was low prior to the beginning of the main spring melt, reached a maximum during the period of maximum flow, and decreased as the summer progressed. A calculation of the seasonal flux indicated that about 40% of the sulphate that flowed out of the watershed was derived from atmospheric sulphate deposited during the previous year. This suggests that more than half of the sulphate deposited in the watershed by atmospheric processes during the previous year was removed during the following summer. Thus sulphate retention in alpine watersheds like Loch Vale is very limited, and changes in sulphate deposition should be quickly reflected in stream chemistry.

### 1. Introduction

The impact of atmospheric deposition of anthropogenically derived sulphur on watersheds has been studied for the past several decades [Krouse and Greenfelt, 1986]. In some cases the extent of the deposition and the degradation of the ecosystem is clearly evident. However, for many watersheds it is difficult to separate the effects of atmospheric sulphur deposition from sulphur mobilized within the watershed by natural processes. Mass balance calculations can indicate the existence of mineralization and release of sulphur from the watershed, but the timing of this release and the residence times of atmospherically derived sulphur in the watershed are generally not well known. Studies of sulphate deposition and outflow have shown that a complicated set of hydrologic factors affect sulphate balances in a watershed [Rochelle et al., 1987; Campbell et al., 1991; Huntington et al., 1994]. Stable isotopes of sulphur are useful in clarifying some of these issues but frequently do not

give conclusive results. Furthermore, they give very little, if any, information on the residence times of atmospherically derived sulphate in the watershed. In certain watersheds the movement of atmospheric sulphur through the hydrosphere can be determined by the use of  $^{35}\text{S}$ , a radioactive isotope ( $t_{1/2} = 87$  days) produced naturally by cosmic ray spallation of argon. The short half-life makes this isotope extremely useful for studying movement of sulphur through the environment on timescales of approximately 1 year. Although there are limitations to its use because of its short half-life and difficulty of measurement, it has been found to be an effective tracer for movement of atmospherically derived sulphate in properly chosen watersheds [Cooper et al., 1991; Michel and Turk, 1996]. It has also been used in studies of runoff of recent deposition from glacial sites [Michel and Naftz, 1995; Cecil et al., 1998] where very little or no interaction is expected with the biota and soils. Sulphur 35 has also been used in watersheds where runoff is rapid and there are very limited biological influences [Burns et al., 1998; Sueker et al., 1999]. This paper describes the use of cosmic ray produced  $^{35}\text{S}$  to follow the pathway of atmospheric sulphur as it migrates through an alpine/subalpine watershed in Loch Vale, Colorado.

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Paper number 1999WR900276.

## 2. Sulphur 35 Systematics

Sulphur 35 is a radioactive isotope of sulphur produced by the collision of cosmic rays with atmospheric argon. The rate of its production depends on the cosmic ray flux which can vary both in time and latitude [Lal and Peters, 1967], but these variations are small relative to uncertainties in deposition [Tanaka and Turekian, 1995]. Sulphur 35 produced in the troposphere will rapidly oxidize to sulphate and deposit on Earth's surface within a few days [Rohde, 1978]. Owing to the slow exchange of air from the upper atmosphere most of the  $^{35}\text{S}$  produced in these atmospheric layers will decay before it can mix into the troposphere and deposit on Earth's surface. However, there are processes that result in the deposition of stratospherically produced  $^{35}\text{S}$  on Earth's surface before it can decay. Sulphate attached to particulates will settle faster than gaseous compounds and may reach the troposphere where it will be rapidly deposited on Earth's surface [Krey and Krawjewski, 1970]. The tropopause in the Northern Hemisphere breaks up every spring because of continental warming, producing an influx of stratospheric air into the troposphere. Furthermore, the tops of some thunderstorms may penetrate above the tropopause, resulting in the scavenging of stratospheric  $^{35}\text{S}$  by precipitation. Thus, even though production is relatively uniform,  $^{35}\text{S}$  deposition rates can show large areal and temporal variations.

Because of the difference in sources, atmospheric concentrations of sulphate and  $^{35}\text{S}$  are not necessarily covariant. In contrast to the cosmic ray generation of  $^{35}\text{S}$ , atmospheric sulphur is derived from a variety of sources on Earth's surface, a large number of which are point sources related to anthropogenic activities. Thus the ratio of  $^{35}\text{S}$  to atmospheric sulphur shows large variations, with the lowest ratios found near the coast and in polluted areas and the highest ratios found in rural continental locations with few agricultural or biological sulphur sources. Once deposited on Earth's surface, atmospherically derived sulphate and  $^{35}\text{S}$  will be affected by geochemical processes in the same manner. Sublimation and evaporation will increase both concentrations equally, and uptake by the biota and adsorption by soils will decrease both concentrations. Differences due to isotopic fractionation are smaller than the uncertainties in the  $^{35}\text{S}$  measurements and can be ignored. However, changes produced by dissolution of minerals and salts or water-rock exchange interactions will produce different changes in the concentrations of sulphate and  $^{35}\text{S}$ . Sulphur derived from minerals will contain no  $^{35}\text{S}$  because of the long residence time in the mineral phase compared to the half-life of  $^{35}\text{S}$ . Thus increases in sulphate concentration produced by mineral dissolution will be distinct from those produced by evapotranspiration of water in that the  $^{35}\text{S}/\text{SO}_4^{-2}$  ratio will decrease during dissolution but remain the same during evaporation. If the atmospheric deposition rate can be determined, the measurement of  $^{35}\text{S}$  presents an excellent opportunity to decouple the movement of sulphur recently derived from the atmosphere from older sulphur added by biogeochemical processes in the watershed. For a watershed like Loch Vale, where the major hydrologic event is snowmelt, it may be possible to determine the  $^{35}\text{S}$  concentration in the snowpack for use as an end member for the initial atmospheric  $^{35}\text{S}$  concentration. Sulphur 35 concentrations can then be measured in other hydrologic reservoirs to determine the fluxes of recent atmospheric sulphur in them.

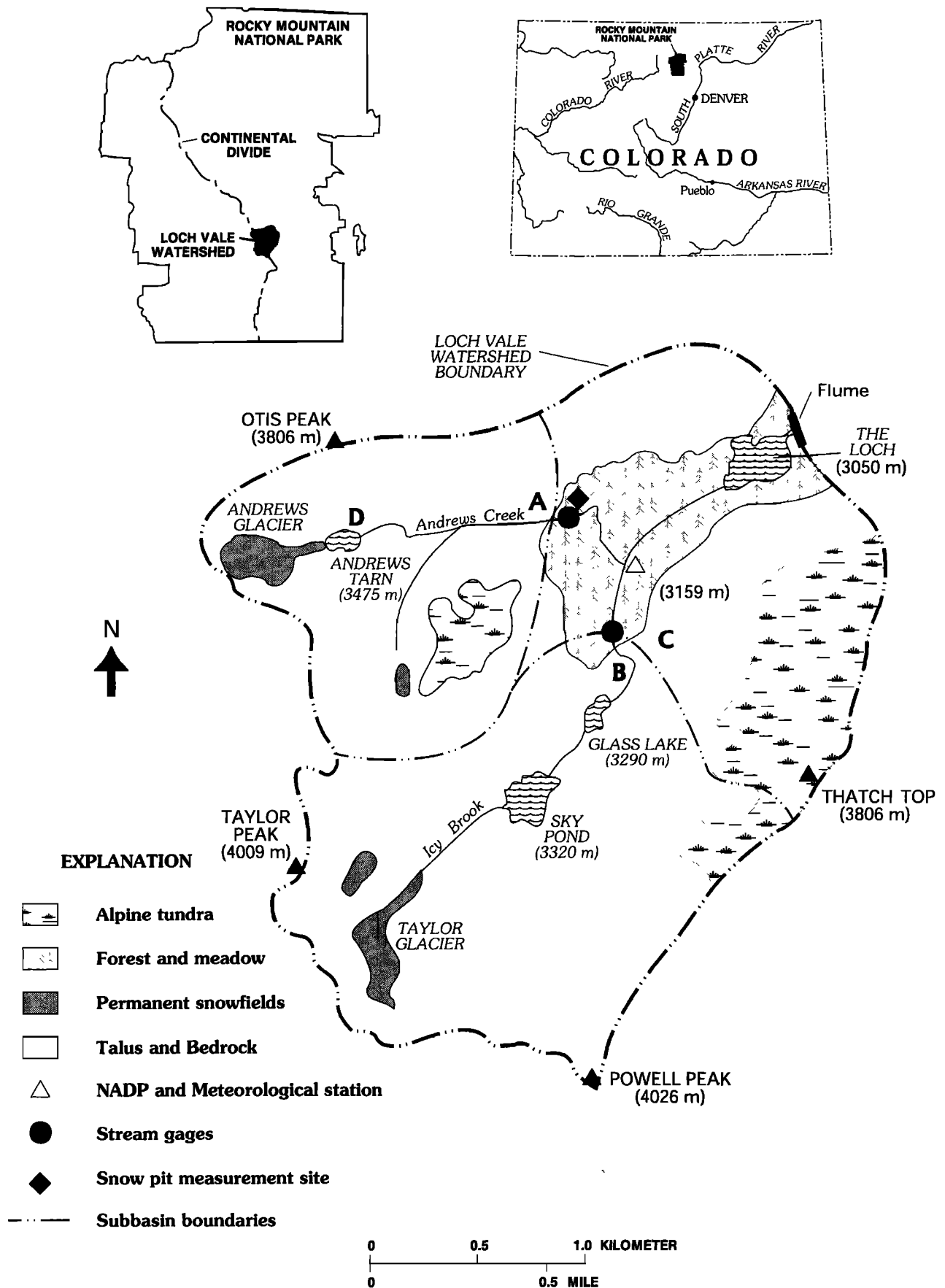
## 3. Hydrogeology of the Loch Vale Watershed

Loch Vale is an alpine/subalpine watershed located in the Front Range of Colorado in Rocky Mountain National Park at an elevation of 3000–4000 m (Figure 1). It abuts the Continental Divide on the west, and the drainage tends to the northeast. It is typical of many of the alpine watersheds of the Rocky Mountains in that there is limited soil development and vegetation [Baron, 1992]. The upper reaches of the watershed above the tree line are composed of rock outcrops, two small glaciers (Taylor and Andrews glaciers), talus fields, and small zones of poorly developed alpine soil along some of the alpine ridges. The lack of significant soil development is attributed to the steeply inclined valley walls that encompass most of the watershed, as well as the relatively short time for soil development (<14,000 years). A discussion of the mineralogy of Loch Vale is given by Mast [1992]. Iron sulphide and carbonate minerals, although present in very small amounts, have an important impact on the sulphate chemistry and alkalinity of the system. Below the tree line a small subalpine spruce and fir forest exists, and along the drainage in the valley floor small wetlands occur in some locations. The predominant vegetation type within Loch Vale is alpine tundra, followed by subalpine forest and wetlands, but more than 80% of the watershed is not covered by any substantial vegetation.

The climate of Loch Vale consists of windy, cold, snowy winters and cool summers. In the winter, precipitation has a predominantly western source, consisting of moisture brought in across the continent from the Pacific region by major storm systems. About 70% of Loch Vale's precipitation occurs as winter (defined as October 1 to May 15) snow, averaging about 79 cm of water per year. Owing to the high winds, blowing snow is also an important factor in the Loch Vale water balance. Redistribution of snow from outside the basin may amount to as much as 10% of the total water input to the watershed. In the spring, precipitation and storms in the Front Range frequently have prevailing wind directions from the east, which can result in transport of sulphur from the urban Denver metropolitan areas. In summer, Loch Vale storms are mostly rain. The main output of water from Loch Vale is runoff, most of which occurs in the summer. Other hydrologic outputs in order of decreasing importance are: sublimation, evapotranspiration, and snow blown out of the watershed [Baron and Denning, 1992]. Seepage through faults in the bedrock appears to play a minimal role in the water balance of Loch Vale.

The two main drainages in the watershed are Icy Brook, flowing to the northeast, and Andrews Creek, flowing almost due east. Icy Brook, the more southerly of the two drainages, originates in the talus and rock fields below Taylor glacier. It flows through Sky Pond and Glass Lake before being joined by Andrews Creek below Glass Lake. Up to the junction of the two streams, Icy Brook has a drainage area of about 330 ha. Andrews Creek flows from Andrews Tarn, beneath Andrews glacier, to its junction with Icy Brook. Unlike Icy Brook, it traverses no permanent lakes in its course, and its drainage is about 180 ha. From the junction of the two streams the combined waters flow into the loch and then out of the drainage. Total area of the drainage at the gage below the loch is 660 ha.

During the winter, measurable flow in Icy Brook ceases to exist, and the lakes become isolated and freeze over. Both streams receive major influxes of water from small springs which flow off the slopes of the watershed during the spring and summer, with the highest flow occurring during late spring



**Figure 1.** Map of the study site. Sampling sites are Andrews Creek (A), Icy Brook (B), Spring 19 (C), and Andrews Spring 1 (D).

and early summer. During peak discharge, residence times of water in the lakes vary from less than a week for the loch and Glass Lake to about 40 days for Sky Pond [Baron, 1992]. During this time the stream chemistry is controlled by snowmelt. Later in the summer, flows decrease and changes occur in the stream chemistry, with concentrations of most constituents increasing.

#### 4. Sampling Program and Analysis

Snow pit samples from the Loch Vale watershed were collected between 1993 and 1997 to obtain an estimate of initial  $^{35}\text{S}$  concentrations in the snowpack prior to snowmelt. All snow samples were full-depth composites. These samples were supplemented by other snow pit samples within the Rocky Mountains that were collected during 1994–1996. Samples of surface waters were collected throughout the spring and summer at the Andrews Creek gaging station during 1995 and 1996. During the spring and summer of 1996, collection sites at the Icy Brook gaging station, Spring 19, and Andrews Spring 1 were added. The two gaging stations on Andrews Creek and Icy Brook are located just prior to the confluence of the two streams (Figure 1). Spring 19 is a spring flowing out of north facing talus into Icy Brook. Andrews Spring 1 flows out of a south facing talus into Andrews Creek through a small wetland.

Stream samples were collected by passing 20 L of water, acidified to pH 3–4, through an ion-exchange resin in the field prior to processing. Snow pit samples, which were occasionally less than 20 L, were frequently brought back to the laboratory for melting. The sulphate was then eluted with about 200 mL of 3 M HCL, and 3 mL of saturated  $\text{BaCl}_2$  was added to the resulting solution to produce a  $\text{BaSO}_4$  precipitate. As sulphate concentrations were extremely low in many of these samples, a sulphate carrier in the form of  $\text{Na}_2\text{SO}_4$  known to be devoid of  $^{35}\text{S}$  was added to the initial sample to obtain an accurate estimate of the recovery of the sample sulphate. The precipitate was then filtered, dried, and counted at the U.S. Geological Survey Tritium Laboratory in Menlo Park, California. Recovery of  $\text{SO}_4^{2-}$  for most samples was greater than 90%. Results of  $^{35}\text{S}$  measurements with  $1\sigma$  counting uncertainties are given in Table 1, both in mBq/L and mBq/mg  $\text{SO}_4^{2-}$ , along with dates of collection and sulphate concentrations. The dates are given in both calendar dates and Julian days (JD), and the latter will be used for graphs and discussion in the text. All  $^{35}\text{S}$  concentrations are corrected for radioactive decay to give the concentration at the date of collection. For purposes of comparison as explained below,  $^{35}\text{S}$  concentrations are also presented as mBq/mg  $\text{SO}_4^{2-}$  and are decay-corrected to JD 90 (corresponding to April 1), which is just prior to the beginning of the spring melt.

### 5. Results

#### 5.1. Sulphate Chemistry at Loch Vale

The two major sources of sulphate input for Loch Vale watershed are atmospheric deposition and oxidation of iron sulphide in the watershed [Mast et al., 1990; Baron et al., 1995]. Some sulphate may be lost as  $\text{H}_2\text{S}$  after sulphate reduction in lake sediments and soil waters. However, most of the  $\text{H}_2\text{S}$  will probably be oxidized in the water column, so very little sulphur is removed from the watershed by loss of  $\text{H}_2\text{S}$  gas. Chemical balances suggest that there has been a net export of sulphur from the watershed over the past few years [Baron, 1992]. One

explanation for the excess sulphur export could be the oxidation or dissolution of sulphur minerals within the watershed. As there are no sedimentary minerals within the watershed, the most likely mineral source for sulphur would be via oxidation of iron sulphide. Stable sulphur isotope data indicate a decrease in  $\delta^{34}\text{S}$  of sulphate as it passes through the watershed. Atmospheric deposition has a  $\delta^{34}\text{S}$  of about +5‰, whereas stream waters have a  $\delta^{34}\text{S}$  in the range of +1 to +3‰ [Brock, 1998]. As reduction of sulphate seems to be unimportant in this catchment, the shift could be explained by oxidation of iron sulphide within the watershed. Another possibility for the source of the excess sulphur is that there may have been a significant decrease in sulphur deposition in the recent past. This would result in washing out of sulphur deposited from previous years when concentrations were higher in incoming precipitation. Both of these processes would release old sulphate, relative to the short half-life of  $^{35}\text{S}$ . Thus both would increase sulphate concentrations and not affect the total activity of  $^{35}\text{S}$  in mBq/L, resulting in a decrease of the activity of  $^{35}\text{S}$  relative to sulphate. Sulphur 35 cannot be used to distinguish between these two processes. Baron et al. [1995] have reported on changes in atmospheric deposition of  $\text{SO}_4^{2-}$  in the Loch Vale watershed from 1984 to 1993. There was a drop in deposition from 1984–1985 to 1987, and it has remained relatively constant since that time. There was no similar drop in outflow of  $\text{SO}_4^{2-}$  during that period, and, in general, outflow of  $\text{SO}_4^{2-}$  correlated much more closely with total water discharge than  $\text{SO}_4^{2-}$  deposition.

Sulphate concentrations in snowpack are generally less than 1 mg/L (Table 1). Although most melt waters have concentrations similar to snowpack, these waters show much larger variations in concentration, with some concentrations reaching close to 10 mg/L. Concentrations in springs and streams in Loch Vale show large variations which are correlated to season and flow. Figure 2 shows sulphate concentrations measured coincident with collection of  $^{35}\text{S}$  samples in 1996 for Andrews Creek, Icy Brook, Andrews Spring 1, and Spring 19. Concentrations tend to be highest in early spring prior to the onset of spring snowmelt (M. A. Mast, personal communication, 1999). As melt progresses and flows increase, concentrations drop rapidly in the runoff, reaching concentrations of less than 1 mg/L during the period of highest flow for Andrews Creek and Icy Brook. Sulphate concentrations stay low in these streams during the summer and start to rise in the early fall. The sulphate concentrations in Spring 19 are much greater than concentrations in the two main streams.

#### 5.2. $^{35}\text{S}$ Chemistry at Loch Vale

The concentrations of  $^{35}\text{S}$  in snow and precipitation represent the baseline for interpretation of  $^{35}\text{S}$  in the other water reservoirs of the Loch Vale hydrologic system. Concentrations are given in Table 1 for  $^{35}\text{S}$  in four snowpack samples collected in Loch Vale between 1993 and 1997, as well as seven snowpack samples collected from other locations in the Rocky Mountains during 1994–1996. Concentrations are also given which are decay-corrected to JD 90 of each year. Snowmelt is the major hydrologic event in Loch Vale and usually begins in early to mid-April. The  $^{35}\text{S}$  concentrations in snowpack on JD 90 (April 1) are therefore considered to represent the input concentration of  $^{35}\text{S}$  from snowmelt for the hydrologic system. The four snowpack samples from Loch Vale have concentrations that range from 15 to 20 mBq/L and 42 to 64 mBq/mg  $\text{SO}_4^{2-}$  and have an average concentration of  $53 \pm 9$  mBq/mg

**Table 1.** Sulphate and Sulphur 35 Concentrations From Snow Samples Within the Rocky Mountain System and Stream Samples Collected During This Study

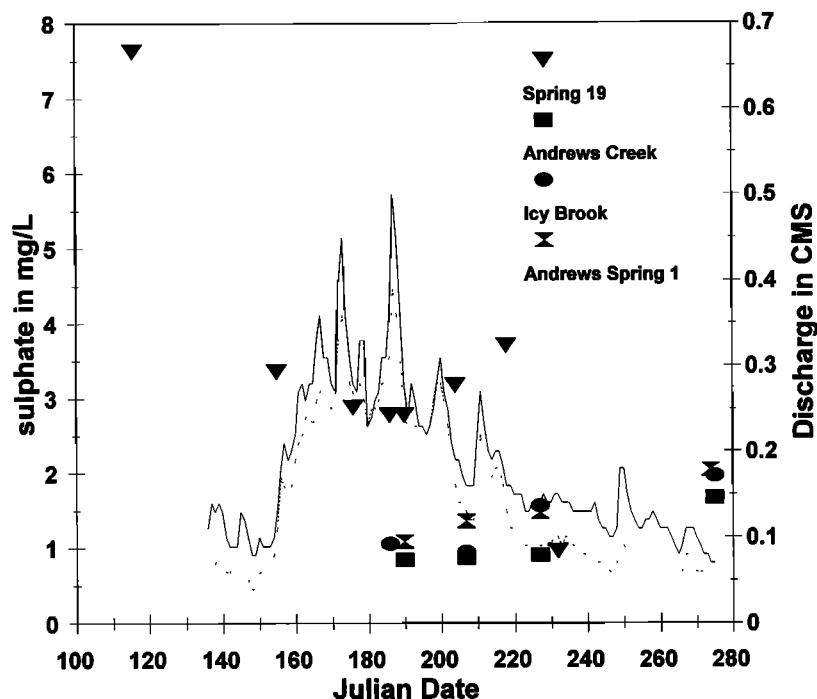
Sample Site and Year	Date JD (Cal)	SO <sub>4</sub> , mg/L	<sup>35</sup> S, mBq/L	<sup>35</sup> S, mBq/mg SO <sub>4</sub>	<sup>35</sup> S, * mBq/mg SO <sub>4</sub>
<b>Snowpack (Loch Vale)</b>					
1993					
Loch Vale Meadow, Colorado	105 (4/15)	0.51	18.8 ± 1.0	37	42 ± 2
1994					
Loch Vale Meadow, Colorado	96 (4/06)	0.29	15.0 ± 3.0	52	55 ± 11
1996					
Loch Vale Meadow, Colorado	99 (4/09)	0.37	17.1 ± 0.5	46	50 ± 2
1997					
Loch Vale Forest, Colorado	105 (4/15)	0.35	19.5 ± 1.4	56	64 ± 5
<b>Snowpack (Other Rocky Mountain Locations)</b>					
1994					
Ned Wilson Lake, Colorado	89 (3/31)	0.34	14.0 ± 4.0	41	41 ± 12
1995					
Buffalo Pass, Colorado	152 (6/01)	0.73	25.0 ± 1.7	34	58 ± 4
1996					
Rabbit Ear Pass 1, Colorado	92 (4/02)	0.38	15.1 ± 0.5	40	40 ± 1
Divide Peak, Wyoming	83 (3/23)	0.33	18.5 ± 0.5	56	53 ± 1
Fremont Pass, Colorado	115 (4/25)	0.22	13.1 ± 0.5	60	74 ± 3
Gypsum Creek, Wyoming	81 (3/21)	0.16	14.4 ± 0.7	90	86 ± 4
Red Mountain, Montana	77 (3/17)	0.13	13.6 ± 0.6	105	94 ± 4
<b>Spring 19</b>					
1996					
1996	116 (4/26)	7.63	37.0 ± 1.6	4.8	6.0 ± 0.3
1996	155 (6/04)	3.36	46.7 ± 1.1	13.9	23.6 ± 0.6
1996	176 (6/25)	2.88	15.0 ± 2.0	5.2	10.5 ± 1.4
1996	186 (7/05)	2.78	14.0 ± 0.8	5.0	11.0 ± 0.6
1996	190 (7/09)	2.78	7.9 ± 2.4	2.8	6.3 ± 1.9
1996	204 (7/23)	3.17	11.6 ± 1.3	3.7	9.3 ± 1.0
1996	218 (8/06)	3.70	5.4 ± 1.9	1.5	4.2 ± 1.5
1996	232 (8/20)	0.96	2 ± 3	2.1	7 ± 10
<b>Andrews Spring 1</b>					
1996					
1996	190 (7/09)	1.09	12.4 ± 0.7	11.4	25.7 ± 1.5
1996	207 (7/26)	1.36	9.6 ± 1.3	7.1	18.4 ± 2.5
1996	227 (8/15)	1.48	8.6 ± 1.1	5.8	17.8 ± 2.3
1996	274 (10/01)	2.04	13.2 ± 1.4	6.5	29 ± 3
<b>Icy Brook</b>					
1996					
1996	186 (7/05)	1.06	15.6 ± 0.7	14.8	32.3 ± 1.4
1996	207 (7/26)	0.95	9.1 ± 1.0	9.6	24.9 ± 2.7
1996	227 (8/15)	1.56	9.2 ± 1.1	5.9	18.1 ± 2.2
1996	275 (10/02)	1.96	6.1 ± 1.3	3.1	14 ± 3
<b>Andrews Creek</b>					
1995					
1995	102 (4/12)	1.99	4.8 ± 1.3	2.4	2.7 ± 0.7
1995	184 (7/03)	1.39	25.5 ± 0.9	18.4	39.6 ± 1.4
1995	193 (7/12)	0.99	21.4 ± 0.7	21.6	50.1 ± 1.6
1995	220 (8/08)	0.90	5.1 ± 0.5	5.7	16.3 ± 1.6
1995	242 (8/30)	0.85	4.0 ± 0.4	4.7	16.3 ± 1.6
1996					
1996	190 (7/09)	0.85	13.7 ± 0.7	16.1	36.5 ± 1.9
1996	207 (7/26)	0.87	9.7 ± 1.1	11.2	29 ± 3
1996	227 (8/15)	0.91	7.8 ± 0.9	8.6	26 ± 3
1996	275 (10/02)	1.67	7.1 ± 1.1	4.3	19 ± 3
1997					
1997	106 (4/16)	1.92	0.0 ± 2.0	0.0	0.0 ± 2.2
1997	239 (8/02)	0.96	2.7 ± 0.4	2.8	9.5 ± 1.4

Dates are given in Julian days (JD) and calendar dates (Cal).

\*Sulphur 35 data are decay-corrected to a date of April 1 of year of sampling. Uncertainties given for <sup>35</sup>S represent 1  $\sigma$  counting uncertainties.

SO<sub>4</sub><sup>2-</sup> when they are age-corrected to JD 90 of the year of deposition. Although snowpack samples from the Rockies have a larger range, a plot of <sup>35</sup>S which is age-corrected to JD 90 versus sulphate concentration (Figure 3) shows a strong relationship between these two components for both the Loch Vale snowpack samples and other Rocky Mountain snowpack samples. The average concentration found for Rocky Mountain snowpack is 60 mBq/mg SO<sub>4</sub><sup>2-</sup> versus the concentration of

53 mBq/mg SO<sub>4</sub><sup>2-</sup> derived from the Loch Vale snowpack. For this study the average concentration of 53 mBq/mg SO<sub>4</sub><sup>2-</sup> for Loch Vale will be used as the starting concentration for <sup>35</sup>S in snowpack as of JD 90. This will be used to determine what we define as “new” sulphate. “New” sulphate is defined as the <sup>35</sup>S concentration in mBq/mg SO<sub>4</sub><sup>2-</sup>, which is decay-corrected to JD 90, divided by 53 mBq/mg SO<sub>4</sub><sup>2-</sup>, representative of original snowpack on JD 90. The “new” sulphate gives an estimate of



**Figure 2.** Sulphate concentrations in mg/L for samples collected in 1996 coincident with the  $^{35}\text{S}$  from the four sampling sites in Loch Vale. Discharge in  $\text{m}^3/\text{s}$  (CMS) is given for Icy Brook (solid curve) and Andrews Creek (dashed curve).

the fraction of sulphate in a sample that had been derived from atmospheric deposition during the past year. Additional  $\text{SO}_4^{2-}$  and  $^{35}\text{S}$  will be deposited in rainfall and by dry deposition throughout the spring and summer. Though no published data are available for  $^{35}\text{S}$  deposited by rains, concentrations of cosmogenically produced isotopes in precipitation are highest in the spring and early summer [Lal and Peters, 1966]. Furthermore, some  $^{35}\text{S}$  in snowpack has been lost because of decay during the winter. Both these factors suggest that  $^{35}\text{S}$  concentrations in spring and summer rains are at or above concentrations found in snowpack. Dry deposition adds both sulphate and  $^{35}\text{S}$ , and it can be expected that the ratio of  $^{35}\text{S}$  to milligrams of  $\text{SO}_4^{2-}$  will be similar to that of summer rains. The additional  $^{35}\text{S}$  added by summer rainstorms and dry fall will increase the concentrations in the streams. When the stream  $^{35}\text{S}$  concentrations are decay-corrected to JD 90, the fraction of “new” sulphate calculated will be higher if  $^{35}\text{S}$  deposited at a later date (i.e., the summer rains or dry fall) is present. This will lead to an overestimate of the fraction of “new” sulphate, so the fraction of “new” sulphate calculated in this report should be considered a maximum value.

Concentrations of  $^{35}\text{S}$  in surface waters show large variations during the year, indicating differences in the ages of sulphate moving through the watershed at various times and locations (Table 1). Frequently,  $^{35}\text{S}$  concentrations were at or near the uncertainty limit, particularly during periods of low flow in early spring and late fall. Highest  $^{35}\text{S}$  concentrations in units of mBq/L are found in Spring 19 where concentrations were near 50 mBq/L in early summer of 1996, well above the typical value found in snowpack. For the main drainages, Icy Brook and Andrews Creek,  $^{35}\text{S}$  concentrations appear to peak during the period of greatest snowmelt in early summer and decrease as the summer progresses and flow rates decrease. Concentrations in Andrews Spring 1 in 1996 were relatively high, both in

terms of mBq/L and mBq/mg  $\text{SO}_4^{2-}$  throughout the summer. All results indicate that during high runoff, a large proportion of the sulphate exiting the watershed was deposited during the previous winter and/or spring (i.e., “new” sulphate). One column in Table 1 gives all  $^{35}\text{S}$  results corrected for decay to JD 90 of the year of collection and these values are used to calculate “new” sulphate.

## 6. Discussion

### 6.1. Spring 19

Spring 19 flows out of a scree field into the Icy Brook system. A series of samples was collected from a period of low flow, prior to the beginning of the 1996 melt season, through August 1996, when the stream ceased to flow. Sulphate concentrations are high (up to 7.6 mg/L) in the early spring and remain at or above concentrations found in the major streams of Loch Vale throughout the summer season (Figure 2). These increased concentrations could be produced by (1) weathering of sulphide minerals within the scree from which the stream emerges, (2) loss of water (and increase of solute concentrations) by sublimation and evapotranspiration, (3) dry deposition which may be more important at this location because of the occurrence of rocks with high surface areas in the catchment of Spring 19, and (4) an ionic pulse produced by preferential elution of ions from the snowpack. Sulphur 35 concentrations in mBq/L were also high in the early spring, exhibiting concentrations 2–3 times above concentrations typically found in snowpack and higher than  $^{35}\text{S}$  concentrations found in the other springs sampled at any time during the year. The high  $^{35}\text{S}$  concentrations found in April and early June of 1996 are a clear indication that at least a fraction of the increase in sulphate concentration is due to loss of snow after deposition, dry deposition, or the existence of an ionic pulse. However, when

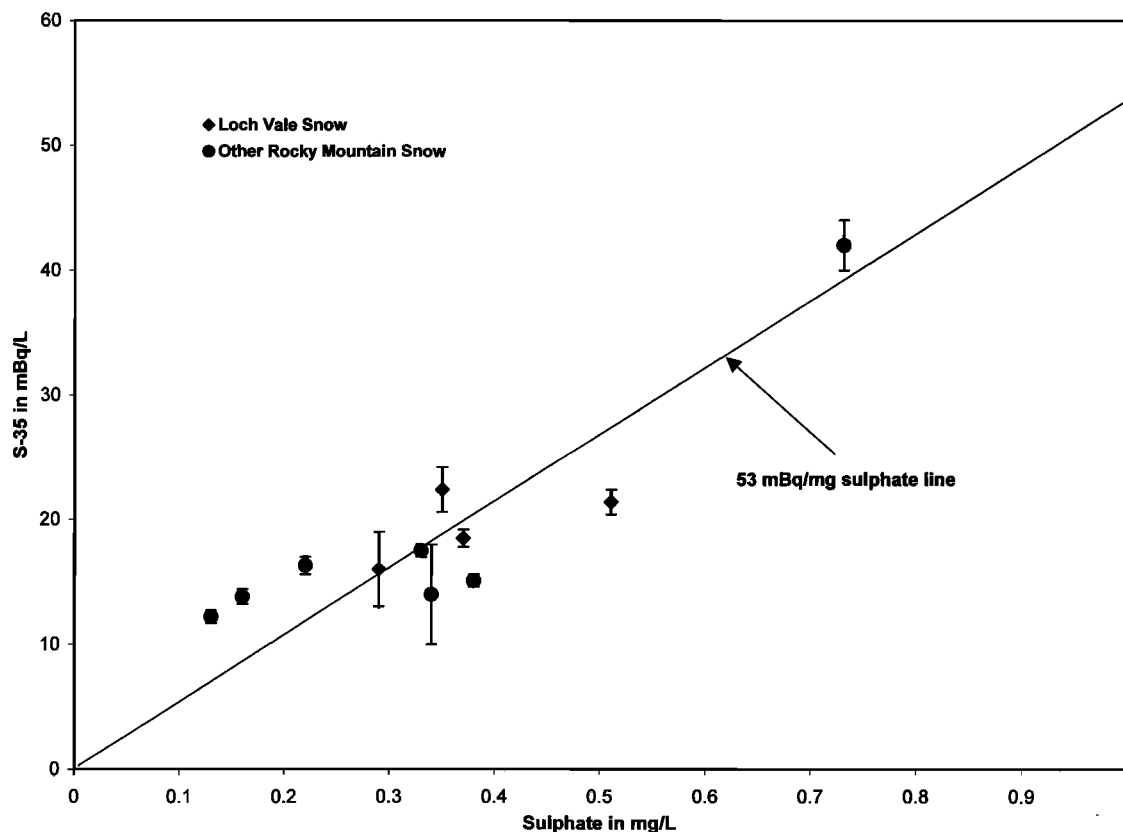


Figure 3. Sulphur 35 in mBq/L which is decay-corrected to JD 90 versus sulphate in mg/L for snowpack samples collected at Loch Vale (diamonds) and other sites in the Rocky Mountain area (circles) for 1993–1997. One sigma counting uncertainties and a line representing the 53 mBq/mg  $\text{SO}_4^{2-}$  used as the initial concentration for JD 90 snowpack are included.

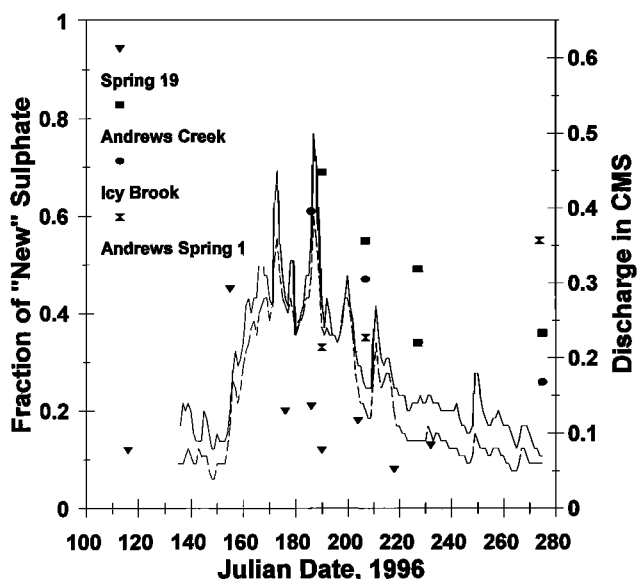
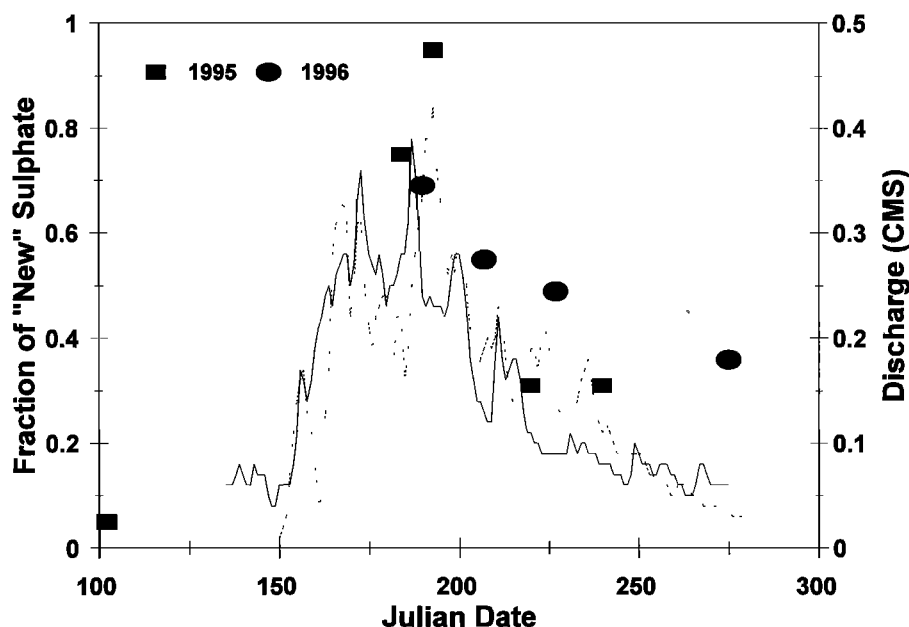


Figure 4. Fraction of “new” sulphate for surface water samples collected in Loch Vale in 1996. “New” sulphate is defined as  $^{35}\text{S}$  concentration mBq/mg  $\text{SO}_4^{2-}$  corrected to JD 90 divided by 53 mBq/mg  $\text{SO}_4^{2-}$ . Discharge in cubic m/s (CMS) is given for Icy Brook (solid curve) and Andrews Creek (dashed curve).

$^{35}\text{S}$  concentrations are converted to mBq/mg  $\text{SO}_4^{2-}$  and are age-corrected to JD 90, they are all lower than the  $^{35}\text{S}$  concentrations in mBq/mg  $\text{SO}_4^{2-}$  typically found in Loch Vale snowpack. Using the average Loch Vale snowpack  $^{35}\text{S}$  concentration of 53 mBq/mg  $\text{SO}_4^{2-}$ , the fraction of “new” sulphate deposited during the 1995–1996 winter can be estimated (Figure 4). From Figure 4 it can be seen that despite the high  $^{35}\text{S}$  concentrations found in Spring 19, it generally has a lower fraction of “new” sulphate than the other sites. The highest fraction of “new” sulphate is found in the sample collected on JD 155. Even at this period,  $^{35}\text{S}$  concentrations suggest that less than half of the sulphate found in the flow of Spring 19 was “new” sulphate. Sulphur 35 concentrations of all other Spring 19 samples indicate that 20% or less of the sulphate comes from the past winter’s atmospheric deposition. The other 80% of the sulphate comes from either oxidation of sulphide minerals, from sulphate deposition in years prior to the last winter where all  $^{35}\text{S}$  has been lost by decay, or a combination of the two sources.

## 6.2. Andrews Spring 1

Andrews Spring 1 is a small spring flowing into Andrews Creek out of a talus field and through a small wetland. Samples were collected during summer and early fall of 1996. Sulphate and other chemical concentrations tend to be higher than at



**Figure 5.** Fraction of "new" sulphate in Andrews Creek samples collected in 1995 (squares) and 1996 (circles). Discharge rate in  $\text{m}^3/\text{s}$  (CMS) is given for 1995 (dashed curve) and 1996 (solid curve).

Andrews Creek but well below concentrations found at Spring 19. Sulphur 35 is present in all samples including the JD 274 sample. Concentrations in  $\text{mBq/L}$  for Andrews Spring 1 neither reach the high levels during early snowmelt or the lower concentrations found in the late summer and early fall of samples from Spring 19. Age correcting the  $^{35}\text{S}$  concentrations in  $\text{mBq/mg SO}_4^{-2}$  to JD 90, the concentrations in Andrews Spring 1 can be compared to the initial snowpack concentration (Figure 4). The results indicate that about 33–55% of the sulphate in Andrews Spring 1 is "new" sulphate. The variations in this percentage are relatively small throughout the summer and actually show an increase for the last sample collected on JD 274. Andrews Spring 1 is a small spring with a small catchment area and may show the influence of the addition of  $^{35}\text{S}$  by summer precipitation to a much greater extent than the larger catchments. This last sample was collected after a major snow-rain event. Thus the increase in "new" sulphate for Andrews Spring 1 may indicate a response to this precipitation event. Also, since the catchment is south facing, melt occurs earlier. Our first sample was collected on JD 190 and may have missed the highest  $^{35}\text{S}$  concentrations which usually occur early in the summer season.

### 6.3. Andrews Creek and Icy Brook

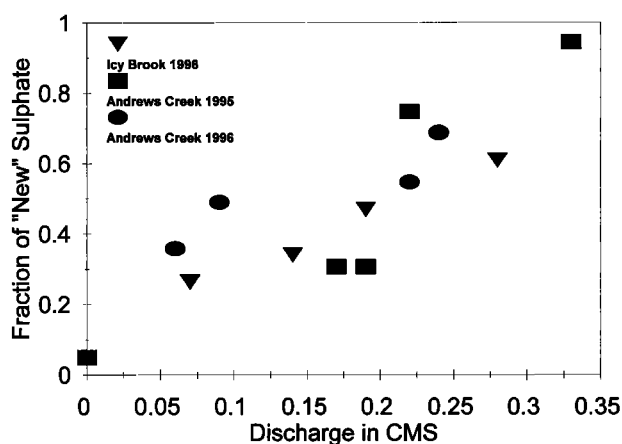
Discharge in these two creeks provides most of the inflow to the loch, especially from the alpine areas. Sulphur 35 samples were collected from Andrews Creek in 1995–1997 and from Icy Brook in 1996. Prior to the beginning of significant melting in early spring, very little  $^{35}\text{S}$ , indicative of "new" sulphate, was found in the streams as noted in the JD 102 of 1995 and JD 106 of 1997 samples (Table 1). With the onset of high flows,  $^{35}\text{S}$  concentrations in  $\text{mBq/L}$  increase and peak in the early summer. Comparison of trends in the two creeks during 1996 shows that concentrations tend to decrease in both creeks as the summer progresses, a decrease that can be partly attributed to decay of  $^{35}\text{S}$  deposited in the winter. When the concentrations are converted to  $\text{mBq/mg SO}_4^{-2}$  and are age-corrected to

JD 90, a decrease in the concentration for  $^{35}\text{S}$  is still present (Figure 4).

It is apparent that a large fraction of sulphate flowing out of the watershed in the early summer melt is derived from sulphate that has been deposited in the system during the previous winter. This is a period when flows are at their highest, and a large fraction of the sulphate and water that exits the watersheds annually does so during this time. The results indicate that despite the existence of wetlands and small lakes, and the probable occurrence of rock-water interactions, atmospheric sulphate moves through the system very rapidly during the melt season. Figure 5 shows the fraction of new sulphate estimated for Andrews Creek for 1995 and 1996. It can be seen that the general trends are the same for both years in Andrews Creek, with a decrease of the fraction of new sulphate after a maximum in the early summer. In 1995, there was a large snowpack, and the melt tended to be later. Thus the highest  $^{35}\text{S}$  concentration occurs later. In 1996, there was more summer rain, which may account for the fact that the apparent fraction of "new" sulphate is higher in late summer in that year. There are variations in the timing of the outflow of "new" sulphate from year to year due to weather patterns (i.e., warm periods with extensive melting or rainfall), but the general trends indicated in Figures 4 and 5 are consistent for the 2 years of this study.

Figure 6 plots the fraction of "new" sulphate versus flow rate measured at the sampling gauges for Andrews Creek in 1995 and 1996 and Icy Brook in 1996. It is apparent that  $^{35}\text{S}$  concentrations and the outflow of "new" sulphate are strongly correlated with high flow produced by melting of the snowpack. The correlation exists between flow rate and "new" sulphate in both years and at both streams. A regression of the data indicates that during the 2 years of this study, for every  $0.1 \text{ m}^3/\text{s}$  (CMS) increase in flow, the fraction of new sulphate increases by approximately 0.2 ( $r^2 = 0.71$ ). This correlation certainly will change from year to year, depending on precipitation amounts and weather factors. However, it appears to be





**Figure 6.** Fraction of "new" sulphate versus discharge in  $\text{m}^3/\text{s}$  (CMS) for Icy Brook (1996) and Andrews Creek (1995–1996).

reliable for these two streams during the period of this study. Thus the spring melt carries with it a large pulse of atmospherically derived sulphate. The results also suggest that any future increases in sulphate deposition will be quickly mobilized during the spring melt and will not interact with the watershed.

## 7. Sulphate Balances

The correlation between "new" sulphate and flow rate for the streams measured in 1995–96 can be used to obtain an estimate of the fraction of the sulphate flowing out of the watershed that is derived from atmospheric deposition during the previous water year. There are daily flow measurements for both streams, and sulphate is measured on a weekly basis for both streams [Campbell *et al.*, 1995]. Sulphate concentrations are linearly interpolated for dates when there are no measurements. The fraction of "new" sulphate is estimated by using the correlation between  $^{35}\text{S}$  and flow rate. The amount of "new" sulphate flowing out of the watershed is then calculated using the daily flow measurements and the estimates of  $\text{SO}_4^{2-}$ . Figure

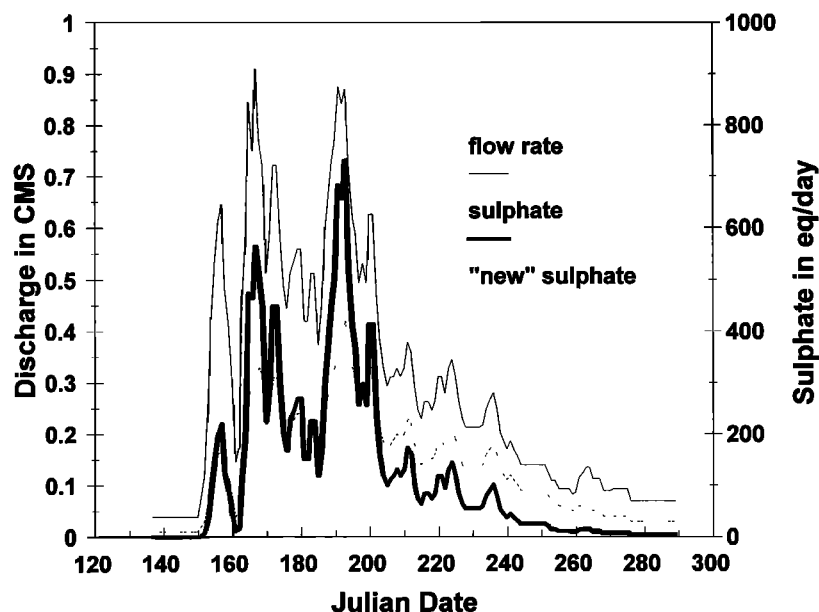
**Table 2.** Fluxes of Sulphate in Loch Vale Watershed

	1995	1996
Andrews Creek		
Deposition	122	136
Outflow	250	230
"New" sulphate	106	82
Icy Brook		
Deposition	122	136
Outflow	...	188
"New" sulphate	...	89

Values are given in equivalents/hectare. Deposition is measured at the National Atmospheric Deposition site in Figure 1. Outflow determined from daily flow data and measured sulphate data (extrapolated for days without data). "New" sulphate is determined from correlation with flow data as explained in text. Ellipsis indicates lack of  $^{35}\text{S}$  measurements.

7 is a plot for Andrews Creek in 1995 of flow, sulphate and modeled "new" sulphate flowing out of the watershed in eq/d. The fraction of "new" sulphate is very low at the beginning and end of the spring and summer season and is highest during the periods of high flow.

The amount of total sulphate and "new" sulphate flowing out of the watershed for the melt season can be calculated and compared to the amount of sulphate deposited in the watershed for that year. Estimates of total sulphate flowing out of the two watersheds are obtained by multiplying daily flow measurements by the sulphate concentration, either measured or interpolated from days when measurements are available. Using estimates of the fraction of "new" sulphate determined from flow data as noted above, the total amount of "new" sulphate flowing out during the summer season can then be calculated. Measurements of deposition obtained at the National Atmospheric Deposition Program (NADP) site located near the confluence of Andrews Creek and Icy Brook are given in Table 2 (M. A. Mast, personal communication, 1999). In both years the total sulphate flowing out of the watersheds for Andrews Creek and Icy Brook was more than 200 eq/ha. For



**Figure 7.** Discharge in  $\text{m}^3/\text{s}$  (CMS) and flux of sulphate and "new" sulphate in Andrews Creek in 1995.

both streams in 1996 and for Andrews Creek in 1995, "new" sulphate represents approximately 40% of the total sulphate flux. Using the sulphate fluxes from the NADP site (122 eq/ha in 1995 and 136 eq/ha in 1996), 60–80% of atmospheric sulphate deposited in the watershed is removed within 1 year. These estimates for removal rates of atmospheric sulphate are qualitative and represent maxima, as the impact of summer rains and dry deposition on  $^{35}\text{S}$  concentrations has not been included. However, they do indicate that a very large fraction of the sulphate that is deposited in the watershed will flow out in less than 1 year. Thus a large fraction of the atmospheric sulphate is not retained in an alpine watershed like Loch Vale but will flow out within 1 year. Changes in atmospheric sulphate deposition in the watershed should have an immediate impact on the sulphate concentrations in the streams and springs of the system. The short residence times obtained also suggest that the excess sulphate leaving the watershed is likely not the result of the washing out of higher sulphate depositions from previous years. It is more likely that the excess sulphate is the result of dissolution or oxidation of mineralized sulphur.

## 8. Conclusions

Cosmogenically produced  $^{35}\text{S}$  has been measured in the Loch Vale watershed to determine timescales for sulphate fluxes within the system. High concentrations of  $^{35}\text{S}$  were seen during the spring and summer in all streams, indicating a rapid movement of atmospherically deposited sulphate through the watershed and into the stream system. The fraction of "new" sulphate (sulphate deposited within the previous year) was estimated for all streams. In the two major streams, Andrews Creek and Icy Brook, it was estimated that approximately 40% of the sulphate flowing out of the watershed originated as atmospheric deposition within the previous year. This represents a large fraction of the sulphate entering the watershed through atmospheric deposition during that period. Thus changes in sulphate deposition will be rapidly reflected in stream chemistry for Loch Vale. The results also demonstrate the value of  $^{35}\text{S}$  as a tracer in watersheds such as Loch Vale. With proper estimates of  $^{35}\text{S}$  deposition by summer precipitation and dry deposition to supplement snowpack measurements, it would be possible to improve estimates of the timescale for sulphate movement through the watershed.

**Acknowledgments.** The authors wish to thank J. Shanley, D. Naftz, N. Peters, L. Cooper, and C. Brock whose insights and suggestions improved the manuscript.

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(Received April 1, 1999; revised September 2, 1999; accepted September 7, 1999.)